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Abstract

An alloying/dealloying technique including stacking rolling was used to fabricate nanoporous architecture on Au sheet surface. Under appropriate conditions, a nanoporous surface layer with a thickness of 150–250 nm was generated. The extended immersion of the sample in the electrolyte (HNO_3) increased the ligament size of the nanoporous architecture up to 41 nm. Cross-sectional observations suggested that the nanoporous surface layer can be seamlessly bonded to the bulk substrate Au. True surface area, which was measured by an electrochemical method, decreased as ligament size increased by the extended immersion. The relationship among surface area, ligament size and volume shrinkage was investigated.

Keywords: Surfaces; Metals and alloys; Porosity

1. Introduction

A nanostructured surface on materials often exhibits novel properties, such as superhydrophobicity [1], structural color [2] and magnetism [3]. It is also well known that a porous surface with controlled pore and ligament sizes enhances the properties of microchannels [4,5], increasing

the interaction between channel wall and internal fluids. Thus, the construction of nanoporous architecture on a material surface may be a key technology for the functional development of materials and/or devices, exhibiting both features of nanostructured and porous surfaces.

On the other hand, nanoporous metals can be fabricated by dealloying binary alloys [6]. When dealloying is combined with a surface alloying technique, the surface of bulk metals can be made nanoporous. A nanoporous surface on a Au film, for example, provides piezoelectricity in an electrolyte [7]. Other alloying/dealloying techniques have also been developed [8,9]. However, no systematic study on a nanoporous surface on metal sheets has been conducted thus far. In this study, a nanoporous surface is fabricated on metal sheets (Au) by an alloying/dealloying technique involving the stacking rolling of pure Au and Ag sheets. The relationship among the surface area, ligament size and thickness of the nanoporous surface layer is investigated.

2. Experimental methods

The process of fabricating a nanoporous surface layer on a Au sheet is schematically shown in Fig. 1. The Au sheet (0.5 mm in thickness) and Ag foil (10 μm in thickness) were stacked and rolled at room temperature to a total thickness of approximately 0.15 mm. Then, annealing at 773 K for 70 min was conducted in air for thermal alloying on the Ag-side surface. Finally, the samples were dealloyed in HNO_3. The following two types of dealloying were conducted at room temperature: electrochemical dealloying, where an electrochemical potential of +1.1 V (vs a saturated calomel electrode (SCE)) is applied in a 0.1 mol/L HNO_3 electrolyte, and free corrosion, where samples are simply immersed in 70 mass% HNO_3. The employed dealloying conditions are listed together with the experimental results in Table 1. The samples were observed with a field-emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectrometer (EDXS) for elemental analyses. Several samples after dealloying were milled with a focused ion beam (FIB) for cross-sectional observation.

Electrochemical measurements including linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were conducted using a potentiostat and a typical three-electrode electrochemical cell with a Pt plate as a counter electrode, an SCE as a reference electrode and a sample as a working electrode.

3. Results and discussion

Microstructures of the Ag-side surfaces after dealloying are shown in Fig. 2. Nanoporous structures with different ligament sizes were observed on the surface. The ligament size of electrochemically dealloyed sample was 5 nm and the smallest in the examined samples, and that of freely corroded samples increased with immersion time, as shown in Table 1. In general, the application of a high electrochemical potential during dealloying leads to a finer nanoporous structure finer than that obtained by free corrosion [10]. A longer immersion time in HNO_3 increases ligament size via diffusion at the solid/electrolyte interface [11]. Thus, the present trend in ligament size evolution is similar to that in the formation of nanoporous Au from homogeneous Au-Ag alloys.

EDXS analysis of these surfaces, however, revealed that the Ag content is as high as 25 atomic% even in the sample immersed for 42 h. The high content of residual Ag is different from the case of nanoporous Au fabricated from homogeneous Au-Ag alloys, where Ag is almost completely removed after a sufficient time of free corrosion [12]. The residual Ag is expected to be segregated at the interface between the nanoporous surface layer and bulk substrate, probably owing to the expected compositional gradient along the thickness direction in the alloyed surface layer before dealloying.

Cross-sectional observations of FIBed samples (exemplified in Figs. 2 (e) and (f)) revealed that the nanoporous surface layers are bonded seamlessly to the underlying Au substrates. The thickness of the nanoporous surface layer was approximately 150–250 nm and smaller for a longer immersion time. A longer immersion time seems to reduce the thickness of the nanoporous surface layer through volume shrinkage [13,14].

The electrochemically active surface area of Au sheets with a nanoporous surface can be measured by CV in a H_2SO_4 electrolyte [13]. The CV curves measured in 0.1 mol/L H_2SO_4 for flat and nanoporous surfaces of the Au sheets are shown in Fig. 3. The apparent exposed area of the samples was 12 mm^2. It can be observed that the current magnitude for the nanoporous surface is much higher than that for the flat Au surface. The increase in current magnitude is attributed to the nanoporous architecture fabricated by the alloying/dealloying technique.

Roughness factor, which is the ratio of the electrochemically active surface area of the nanoporous Au surface to that of the flat Au surface, can be estimated using the charge associated with the reduction of adsorbed oxygen by the following equation [13]:

$$A_{np}/A_{flat} = Q_{OC,np}/Q_{OC,flat}, \qquad (1)$$

where A is the surface area and Q_{OC} is the charge associated with the reduction of adsorbed oxygen. The subscripts "np" and "flat" indicate that the variables are for the nanoporous and flat Au surfaces, respectively. Q_{OC} can be calculated using the cathodic peak between +0.6 and +1.05 V (vs SCE) after correction for double-layer charging. The calculated roughness factors are listed in Table 1. Also, as shown in Fig. 4, roughness factor increased up to 89 with a decrease in ligament size. Line fitting by a least-squares method revealed that the roughness factor is proportional to the 1.4th power of the reciprocal of the ligament size.

Assuming the Gibson-Ashby unit cell model [14] that gives general pore characteristic effects on various properties, the surface area (S) per volume of porous materials can be expressed as

$$S \propto \frac{lt}{l^3} = \left(\frac{t}{l}\right)^2 \frac{1}{t} = \frac{\rho}{\rho_s}\frac{1}{t}, \qquad (2)$$

where l and t are the edge length and edge thickness, respectively, and ρ/ρ_s (= $(t/l)^2$) is the relative density of the porous material. Equation (2) can also be presumed by the simple dimensional analysis. This equation indicates that the surface area (and thus roughness factor) is proportional to the reciprocal of the ligament size, if the relative density is constant; however, the exponent that correlates the roughness

factor and ligament size is −1.4. This difference between the theoretical and experimental exponents is likely due to volume shrinkage (Figs. 2 (e) and (f)). That is, the actual volume of the nanoporous surface layer decreases as the immersion time increases, which then reduces the total surface area.

The CV measurement revealed that the present alloying/dealloying process increases the true surface area of the Au sheet by up to 90; however, the roughness factor is not as high as the values reported in the literature [8,9]. Jia et al. [8] reported a high roughness factor of 560 in nanoporous Au despite its coarse structure having a typical ligament size of approximately 100 nm. Huang and Sun [9] also revealed that the roughness factor of nanoporous Au can be as high as 214. This is probably due to the difference in thickness between the surface nanoporous layers. The thicknesses of nanoporous surface layers in these previous studies are as large as approximately 5 μm [8] and 4 μm [9] (estimated from the micrographs shown in the literature), which are much larger than the thickness of the present surface nanoporous layer (150–250 nm, as shown in Figs. 2 (e) and (f)). Thus, the thickness of the nanoporous surface layer, as well as its ligament and pore sizes, must be considered when one discusses the roughness factor of a nanoporous metal.

Acknowledgements

M. H thanks The Japan Society for Technology of Plasticity for the financial aid (Mitsui Seimitsu Bisai Kakou Kenkyu Shoreikin). Part of this work was supported by JSPS KAKENHI (22656155).

[1] Lau KKS, Bico J, Teo KBK, Chhowalla M, Amaratunga GAJ, Milne WI et al. Nano Lett 2003;3:1701–5.

[2] Kinoshita S, Yoshioka S. ChemPhysChem 2005;6:1442–59.

[3] Barth JV, Costantini G, Kern K. Nature 2005;437:671–9.

[4] Thybo S, Jensen S, Johansen J, Johannessen T, Hansen O, Quaade UJ. J Catal 2004;223:271–7.

[5] Wan YSS, Chau JLH, Gavriilidis A, Yeung KL. Chem Commun 2002;878–879.

[6] Erlebacher J, Aziz MJ, Karma A, Dimitrov N, Sieradzki K, Nature 2001;410:450–3.

[7] Kramer D, Viswanath RN, Weissmüller J. Nano Lett 2004;4:793–6.

[8] Jia F, Yu C, Ai Z, Zhang L. Chem Mater 2007;19:3648–53.

[9] Huang JF, Sun IW. Adv Funct Mater 2005;15:989–94.

[10] Parida S, Kramer D, Volkert CA, Rösner H, Erlebacher J, Weissmüller J. Phys Rev Lett 2006;97:035504.

[11] Ding Y, Kim YJ, Erlebacher J. Adv Mater 2004;16:1897–900.

[12] Wittstock A, Neumann B, Schaefer A, Dumbuya K, Kübel C, Biener MM et al. J Phys Chem C 2009;113:5593–600.

[13] Trasatti S, Petrii OA. J Electroanal Chem 1992;327:353–76.

[14] Gibson LJ, Ashby MF, Cellular solids: structure and properties, 2nd ed., Cambridge: Cambridge University Press; 1997.

Tables

Table 1 Conditions of fabrication of nanoporous surface layer on Au sheet by alloying/dealloying technique. Ligament sizes and roughness factors of nanoporous surface layers are also listed.

Dealloying method[a]	Ligament diameter (nm)	Roughness factor	Label in Fig. 3
EC, 15 min	5	89	a
FC, 15 min	16	36	b
FC, 3 h	30	6	c
FC, 42 h	41	5	d

[a] EC = electrochemical dealloying in 0.1 mol/L HNO_3 at a potential of +1.1 V vs saturated calomel electrode; FC = free corrosion in 70 mass% HNO_3. Dealloying was conducted at room temperature.

Figure captions

Fig. 1 Schematic illustration of fabrication of metallic sheet with nanoporous surface by stacking rolling and dealloying.

Fig. 2 Scanning electron micrographs of nanoporous Au surfaces. Dealloying was conducted by (a) electrochemical dealloying and (b) free corrosion for 15 min, (c) free corrosion for 3 h and (d) free corrosion for 42 h. The panels (e) and (f) are scanning electron micrographs of FIBed and tilted samples (free corrosions for (e) 15 min and (f) 42 h) presented to show the cross section.

Fig. 3 Cyclic voltammetric curves for nanoporous and flat Au surfaces. The labels a-d are explained in Table 1.

Fig. 4 Relationship between roughness factor and ligament size of nanoporous Au surface.

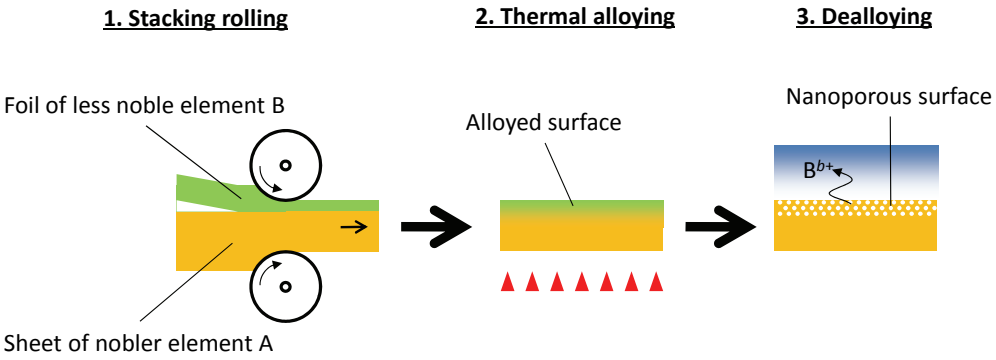

Fig. 1

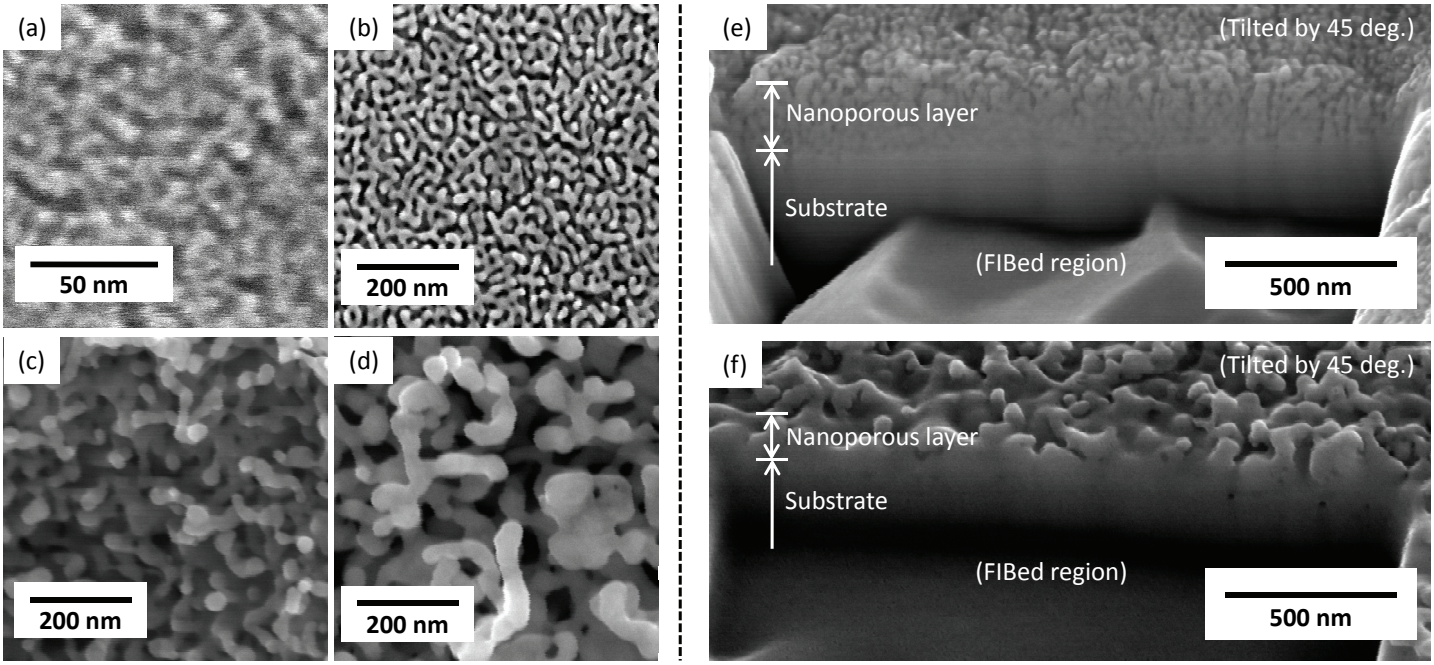

Fig. 2

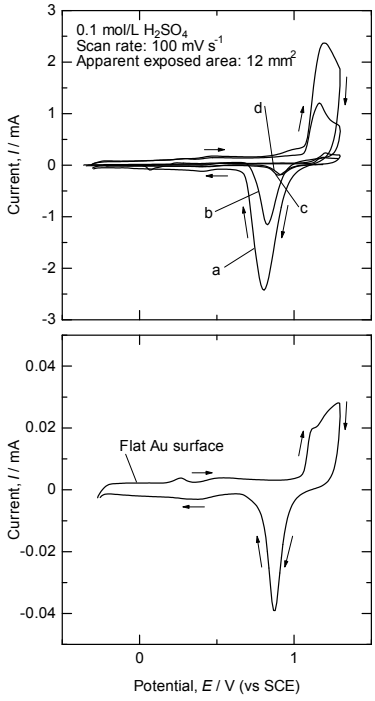

Fig. 3

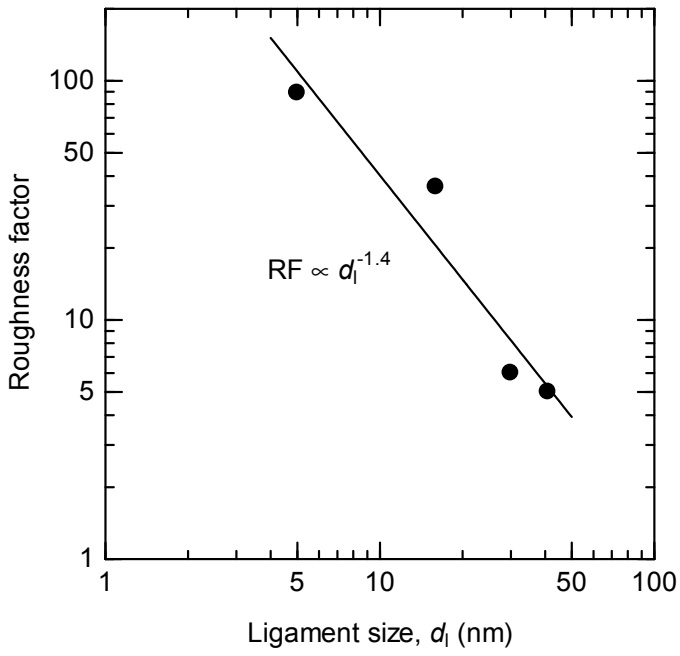

Fig. 4